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Solvation of hydrocarbons in aqueous-organic mixtures

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ABSTRACT

We study the solvation of two hydrocarbons, n-octane and toluene, in binary mixtures of water with organic cosolvents. Two polar aprotic cosolvents that are miscible with water in any proportions, acetonitrile and acetone, were considered. We determine the magnitudes of thermodynamic functions of dissolution and solvation at T = 298.15 K in the mixtures with various compositions. Solution calorimetry was used to measure the enthalpies of solution, and GC headspace analysis was applied to obtain limiting activity coefficients of solutes in the studied systems. For the first time, the enthalpies of solution of alkane in the mixtures with high water content were measured directly. We observed well-pronounced maxima of the dependencies of enthalpies of solvation from the composition of solvent and no maxima for the Gibbs free energies of solvation. Two factors are concluded to be important to explain the observed tendencies: high energy cost of reorganization of binary solvent upon insertion of solute molecules and preferential surrounding of hydrocarbons with the molecules of organic cosolvent. Enthalpy-entropy compensation leads to a steady growth of the Gibbs free energies with increasing water content. On the other hand, consideration of the plots of the Gibbs free energy against enthalpy of solvation clearly shows that the solvation properties are changed dramatically after addition of a rather small amount of organic cosolvents. It is shown that they suppress the hydrophobic effect very effectively even at low concentration, and acetonitrile suppresses the hydrophobic effect less than acetone.

1. Introduction

The interest to binary and especially to mixed aqueous-organic solvents is due to a number of reasons. First, the physico-chemical properties of these solvents can be controlled by variation of their composition. In addition, binary solvents may have such properties that no one individual solvent has. For example, in an aqueous-organic media, both slightly polar organic molecules and inorganic salts can be soluble, which makes them suitable for homogeneous chemical syntheses. Unusual regioselectivity and reactivity were observed in such solvents [1]. Aqueous-organic mixtures are used for synthesis of peptides [2] and preparation of nanomaterials [3]. They are also widely used in industrial and laboratory separation processes. In particular, HPLC, one of the most general and widely applied methods of qualitative analysis and separation of substances, is impossible to imagine without using binary solvent systems. They are also interesting for pharmaceutical chemistry in order to solubilize drugs that are poorly soluble in water [4,5]. Many interesting phenomena have been found in the studies of proteins and enzymes in aqueous-organic solvents. Addition of organic solvents to aqueous solutions of proteins usually leads to their destabilization, denaturation and decrease of enzymatic activity, but there are some evidences of enhancing the rate and selectivity of enzyme-catalyzed reactions [6,7].

The solvent effect on reactivity of dissolved molecules, their solubility and ADME (Absorption, Distribution, Metabolism, and Excretion in living organisms) properties is determined by the value of the chemical potential (partial molar Gibbs free energy) change upon dissolution of a substance. In turn, the Gibbs free energy consists of the enthalpy and entropy components. We can determine the thermodynamic functions of dissolution and solvation in binary solvents from the experimental studies or using predictive thermodynamic models, if the last ones are enough precise. This knowledge can help us to adjust the reactivity and solubility of substances in various applications and to optimize separation processes.

Despite their importance, thermodynamic properties of dilute solutions in mixed solvents are way much less studied experimentally than in individual solvents. There are relatively more data for solvation in (water + alcohol) mixtures [8] and less for other organic solvents that are infinitely miscible with water. This is in part because of a large number of compositions for each mixture that should be considered. Thermochemical studies of dissolution in binary solvents reveal interesting features [9].

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